Preparation and Uncertainty Calculations for the Molality-Based Primary Standards for Electrolytic Conductivity

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Abstract

The National Institute of Standards and Technology (NIST) will no longer produce the electrolytic conductivity Standard Reference Materials® (SRMs ®) 3194, 3195, and 3196 (10 000 µS/cm, 20 000 µS/cm, and 100 000 µS/cm). The SRMs will be replaced by three molality-based primary standards, which have known molalities (0.01 mol/kg, 0.1 mol/kg, and 1.0 mol/kg) and conductivities (1409.33 µS/cm, 12 825.7 µS/cm, and 108 621 µS/cm, respectively). These primary standards can be prepared accurately following the instructions given in the article.

Key Words

electrolytic conductivity, molality, primary standards, solution preparation, SRM

Introduction

The conductivities of molality-based primary standards at 25 °C are provided in an IUPAC technical report [1]. In light of the IUPAC technical report, the National Institute of Standards and Technology will cease production of Standard Reference Materials® (SRMs®) 3194, 3195, and 3196 (10 000 µS/cm, 20 000 µS/cm, and 100 000 µS/cm) [2]. The primary standards have conductivities (Table 1) that bracket the range of these SRMs and, therefore, the production of these SRMs is no longer necessary. In place of these SRMs, NIST-traceable

conductivity standards can be prepared accurately, with a relative combined standard uncertainty of about 0.02 %, using any issue of SRM 999 (KCl) and water (> 16 MΩ·cm water).

This article describes the method for preparation of the molality-based primary standards that are traceable to the Système International d'Unités (SI) [1]. The uncertainty components are listed and a sample calculation is provided. The combined standard uncertainty obtained using the method described in this article should be included in the overall uncertainty of the cell calibration, along with other components of the uncertainty (e.g. resistance and temperature).

These instructions are intended for preparation of the highest accuracy standards.

Preparation of the primary standard

Primary standards are prepared using SRM 999 (KCl) and high-purity water (κ > 16 MΩ·cm). High-purity water may be obtained using a point-of-use water system that is specified as producing 18 MΩ·cm water at delivery and is maintained according to the manufacturer's specification. The resistivity of the water will decrease to ≈ 1 MΩ·cm ($\kappa \approx$ 1.1 μS/cm) due to dissolution of atmospheric CO_2. The increase in κ from CO_2 is included in κ of the primary standards listed in Table 1.

Each solution must be prepared to within ± 0.005 % of the desired molality (0.010 000 mol/kg, 0.100 00 mol/kg, or 1.0000 mol/kg). The molality of KCl, b_{KCl}, is calculated by equation 1,

$$b_{KCl} = \frac{m_{KCl}\, w_{KCl}\, v_{KCl}\, 1000}{M_{KCl}\, v_{H_2O} m_{H_2O}} \qquad (1)$$

where w_{KCl} is the purity (mass percent) of the KCl, 1000 is a conversion factor (g/kg), M_{KCl} is the molar mass of KCl (g/mol) [3], and m_{KCl} and m_{H_2O} are the masses in air (g), not corrected for air buoyancy, of KCl and water, respectively. The buoyancy corrections, v_{KCl} and v_{H_2O}, which are used to correct for the effects of air buoyancy, are calculated by equation 2,

$$v_x = 1 + \rho_{air}\left(\frac{1}{\rho_x} - \frac{1}{\rho_w}\right) \quad (2)$$

where x refers to either KCl or H_2O, ρ_{air} is the density of air [4], ρ_x is the density of x (g/cm^3) [5], and ρ_w is the density of the weights (g/cm^3). All masses must be recorded to at least 5 significant figures. The balances must have sufficient resolution and be calibrated appropriately (e.g. when weighing a mass of ≈ 250 g, the balance must have a resolution of, and be calibrated to, 0.01 g; when weighing a mass of ≈ 2000 g, the balance must have a resolution of, and be calibrated to, 0.1 g).

Procedure

1) All glassware, plasticware, weighing boats, and spatulas should be thoroughly cleaned to remove contaminants from the previous sample. Then, rinse and soak all glassware, plasticware, weighing boats, and spatulas with water at least three times, then dry in a clean air hood or oven.
2) Determine the amount of solution needed for 1 conductivity measurement (usually 250 g – 500 g). Plan to prepare slightly more solution than is actually required: m_{H_2O}, target.

3) Add the nominal amount of KCl needed to a metal weighing boat. The nominal amount of KCl may be determined using equation 1 and solving for m_{KCl} (for this step only, assume $v_{KCl} = v_{H_2O} = 1$).
4) Determine the mass in air of the weighing boat filled with KCl: $m_{(KCl + wb)}$.
5) Empty the KCl from the boat into the plastic bottle (no KCl should be on the outside of the bottle). Do not rinse the boat.
6) Record the mass in air of the weighing boat: m_{wb}. Any KCl remaining in or on the weighing boat is included in m_{wb}.
7) Calculate m_{KCl}: $m_{KCl} = m_{(KCl + wb)} - m_{wb}$.
8) Calculate v_{KCl} and v_{H_2O} using Eq. 2.
9) Place the bottle, now containing KCl, on a larger capacity balance and tare the balance.
10) Determine the mass of water needed to yield the target molality using Eq. 1: m_{H_2O}, target.
11) To the bottle containing KCl, add water to within 0.005 % of the target m_{H_2O} and record the mass in air of water added, actual m_{H_2O}. The actual m_{H_2O} must be within 0.005 % of the calculated target m_{H_2O} from step 10 or the solution must be discarded.
12) Shake calibrant periodically for 30 minutes to facilitate equilibration with CO_2. The standard will have a value of κ that includes the solvent contribution (1.1 µS/cm) [1].

Uncertainty in the conductivity, κ, of the standard

The uncertainty components for κ and their source references for the preparation of a standard at NIST are described in Table 2. In general, the contribution from each component of the uncertainty is obtained from literature sources, instrument manuals, and calculations using

the data collected during the solution preparation.

In many cases, the literature source or instrument manual is not clear as to the meaning of the cited uncertainty. Three cases are described below:

1) If the uncertainty is specified as a standard deviation or a standard uncertainty, use the value directly.

2) If the uncertainty is specified with a given confidence (e.g. 95 % confidence interval, 99 % confidence interval), the uncertainty should be divided by the coverage factor, k, if given. If k unspecified, then the uncertainty should be divided by 2 for the case of 95 % confidence or divided by 2.58 for the case of 99 % confidence.

3) If the uncertainty is specified and the distribution stated (e.g. normal, uniform), the uncertainty should be used directly if the distribution is normal or divided by $3^{½}$ if the distribution is uniform.

4) If the uncertainty is specified without any other information, the user must make a judgement as how to best convert the specified value to a standard uncertainty [7].

The standard uncertainties are then summed in quadrature to obtain the combined uncertainty in κ.

The uncertainty calculation described below (see: Example Calculation) may be performed for any laboratory, using the appropriate values for the laboratory in which the solution preparation took place. The values and uncertainties obtained from the literature (in M_{KCl}, ρ_{air}, v_{KCl}, v_{H_2O}, ρ_{KCl}, ρ_{H_2O}, κ based on the literature value, and κ from CO_2 fluctuations) will be the same in any laboratory. The uncertainty in κ from CO_2 fluctuations is an estimate of the variation in κ resulting from variations in CO_2 within the laboratory and between laboratories. The uncertainties obtained from instrument manufacturers (for m_{KCl} and m_{H_2O}) or

from measurement data (for solution preparation) will vary between laboratories, but may be determined with ease.

The uncertainty as discussed in this article is meant to provide the reader with a basic understanding of the uncertainty components in preparing the primary standard. For details on determining uncertainties (e.g. coverage factors, distributions, standard uncertainties, and combined uncertainties) consult Refs. [7,8].

Example Calculation for b_{KCl} = 0.01 mol/kg

The following example calculation uses values representative of those applicable to the measurements at NIST.

Part 1: Prepare 320 g *of the standard having* κ = 1409.33 µS/cm (b = 0.01 mol/kg) *and calculate the actual molality (Table 2)*

1) Using equation 1 (for this step only, assume $v_{KCl} = v_{H_20} = 1$), determine the nominal amount of KCl needed to prepare 320 g of the 0.01 mol/kg: target m_{KCl} = 0.238 608 g.

2) Add the nominal amount of KCl to the bottle as described above: $m_{(KCl + wb)}$ = 5.029 700 g, m_{wb} = 4.790 713 g, actual m_{KCl} = 0.238 987 g.

2) Calculate v_{KCl} and v_{H_2O} using Eq. 2, where ρ_w = 8 g/cm^3 for stainless steel weights: v_{KCl} = 1.000 44 and v_{H_2O} = 1.001 03.

3) Calculate the mass of water needed by solving Eq. 1 for m_{H_2O}: m_{H_2O} = 320.320 g, target.

4) Add water to within 0.005 % of the amount needed and record: m_{H_2O} = 320.336 g, actual.

5) Calculate b_{KCl} using Eq. 1: b_{KCl} = 0.009 999 5 mol/kg.

Part 2: Determine the standard uncertainty of the molality of the standard (Table 3)

1) Calculate the relative uncertainty in v_{KCl} and v_{H_2O} by determining the change in v_{KCl} and v_{H_2O} when ρ_{air} changes 1 %: 0.000 41 and 0.0010 %, respectively.
2) Calculate the uncertainty in m_{H_2O} based on a balance uncertainty of 5 mg (stated by the manufacturer). The uncertainty is assumed to have a uniform probability distribution: 2.9 mg (0.000 90 %, relative).
3) Calculate the uncertainty in m_{KCl} based on the balance uncertainties for $m_{(KCl + wb)}$ and m_{KCl} of 5 µg (stated by the manufacturer). The uncertainty for each is assumed to have a uniform probability distribution (2.9 µg) and the two uncertainties are summed in quadrature: 4.1 µg (0.0017 %, relative).
4) Convert the uncertainty in M_{KCl} to a relative uncertainty: 0.000 94 %.
5) Calculate the combined standard uncertainty in the molality of the standard by summing in quadrature the relative standard uncertainties discussed in 1-4 in this part of the calculation. (see: Table 3). The relative standard uncertainty in w_{KCl} is included in Table 3 because the data may be taken directly from the certificate for the SRM [6].

Part 3: Determine the Standard Uncertainty of the Conductivity of the Primary Standard (Table 4)

1) Calculate the standard uncertainty in κ due to the molality, using the assumption that κ is proportional to b_{KCl}: 0.0048 %, relative (0.07 μS/cm).
2) Add in quadrature the absolute standard uncertainties in κ due to molality, CO_2 (see Table 2), and the literature value of κ (see Table 1) to obtain the combined standard uncertainty for κ of the primary standard.

For additional information or assistance, contact

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Table 1. Conductivity of the Primary Standard at 25 °C [1]

Molality of KCl, b_{KCl}/(mol/kg)	**κ^a**	**Standard Uncertainty**
0.01	1 409.33	0.21
0.1	12 825.7	2.6
1.0	108 621	22

[a]including a solvent conductivity of 1.1 µS/cm

Table 2. Uncertainty Components for Example Calculation

Component	**Value**	**Standard Uncertainty**	**Source of Standard Uncertainty** (note A)
w_{KCl}	99.9817 %	0.0042 %	Ref. [6] (note B)
M_{KCl}	74.5513 g/mol	0.7 mg/mol	Ref. [3] (note C)
m_{KCl}	0.238 987 g	4.1 µg	5 µg (note d and note E)
ρ_{air}	0.001 173 g/cm^3	6.8 µg/cm^3	Ref. [4] (note D)
ρ_{KCl}	1.984 g/cm^3	negligible	assumed
ρ_{H_2O} (at 21.6 °C)	0.997860 g/cm^3	negligible	assumed
ρ_w	8 g/cm^3	negligible	assumed
κ (literature value)	1409.33 µS/cm	0.21 µS/cm	Ref. [1] (note B)
CO_2 effect on κ	1409.33 µS/cm	0.115 µS/cm	0.2 µS/cm (note D)

note A: for details regarding confidence intervals and distributions, consult Ref. [6,7].

note B: value listed at 95 % confidence interval and divided by 2 to normalize.

note C: value listed at 99 % confidence interval and divided by 3 to normalize.

note D: value is treated as uniform probability distribution and divided by $3^{½}$.

note E: Uncertainties in $m_{(KCl + wb)}$ (2.9 µg) and m_{wb} (2.9 µg) are summed in quadrature.

Table 3. Determine the Combined Standard Uncertainty in the Molality

Component	Standard Uncertainty	Relative Standard Uncertainty/%
w_{KCl}	0.0042 %	0.004 2
M_{KCl}	0.7 mg/mol	0.000 94
m_{KCl}	4.1 μg	0.001 7
m_{H_2O}	2.9 mg	0.000 91
v_{KCl}	2.6×10^{-6}	0.000 41
v_{H_2O}	5.9×10^{-6}	0.001 0
Combined Standard Uncertainty:		**0.004 8**

Table 4. Determining the Standard Uncertainty of the Conductivity

Component	**Standard Uncertainty/(μS/cm)**
Molality	0.07
CO_2	0.12
Literature value of κ	0.21
Combined standard uncertainty:	**0.25**